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THE ACTION OF VARIOUS ANHYDROUS CHLORIDES ON TELLURIUM TRIOXIDE

by

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A Thesis Submitted for the Degree of

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Historical Considerations.

The following experiments were made to determine the action of various anhydrous liquid chlorides, such as sulphur monochloride, thionyl chloride, sulphuryl chloride, phosphorus trichloride, phosphorus oxychloride, arsenic trichloride and antimony pentachloride upon tellurium trioxide.

Previous investigators worked with tellurium and tellurium dioxide. Berzelius[1] investigated the action of chlorine on tellurium and found that it gave tellurium dichloride and tellurium tetrachloride. Professor V. Lenher[2] studied the action of various anhydrous liquid chlorides upon tellurium and tellurium dioxide. Bela von Horwath[3] continued this general line of work and found that when sulphur(yl) and thionyl chlorides act upon tellurium, tellurium tetrachloride is given

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1- Berzelius- Pogg. Anal. 28 392.
2- Lenher- J.A.C.S. 24 188 - (1902)
" " " " " 30 737 - (1908)
3- Bela von Horwath. Z. Anorg. Ch. 70 408.

Preparation of the Telluric Acid and Tellurium Trioxide.

The tellurium used was the crude metal as sold by the Raritan Copper Works, Perth Amboy, N. J. The metal was broken into small pieces and dissolved by adding small amounts of aqua regia. When the action of the acid ceased, it was poured off into a large evaporating dish and fresh acid added to the tellurium. This process was repeated until all the tellurium was in solution. The acid solution was evaporated to dryness and the residue treated with concentrated nitric acid and evaporated to dryness the second time, in order to convert it to the basic nitrate to tellurium.

This basic nitrate was covered with 1:1 nitric acid and a slight excess over the calculated amount of chromium trioxide was added to convert it to telluric acid ($H_2TeO_4 \cdot 2H_2O$ or sometimes written H_6TeO_6) Staudenmaier.[1] The solution was concentrated on a steam bath until crystals began to form, then cooled and the supernatent liquid poured from the crystals. The solution was repeatedly concentrated until no more telluric acid crystals were given.

The crystals were washed with dilute nitric acid to remove most of the chromium trioxide and chromium nitrate and were dissolved in the least amount of warm water. Any insoluble material was filtered off. Concentrated nitric acid was slowly added with constant stirring in order to precipitate the telluric acid and keep the chromium nitrate in solution. On allowing the mixture to cool almost all the telluric acid crystallized out of the solution. The liquid was poured off

1- Staudenmaier. Z. Anorg. Chem. 10 189.

and the crystals were well drained from the solution and this process of dissolving and crystallizing repeated five times. The final product gave pure white crystals of telluric acid and a colorless solution.

These crystals were washed with a small amount of cold water and evaporated to dryness on a steam bath. The material was stirred constantly, while drying, to facilitate the removal of the nitric acid and give the telluric acid as a fine powder.

Small amounts of the telluric acid were spread out in a thin layer on a large cover glass and heated very carefully to a temperature between 265-270°. At a temperature of 160° the telluric acid gives up two molecules of water ($H_2TeO_4 2H_2O = H_2TeO_4 + 2H_2O$) and at the higher temperature the H_2TeO_4 goes to tellurium trioxide and water. The tellurium trioxide is a light yellow colored and is called the anhydride of telluric acid with the formula TeO_3.

Care was taken in heating the telluric acid, for with temperatures above 270° the tellurium breaks down into tellurium dioxide and oxygen. There was always a small amount of tellurium dioxide produced which was removed by boiling for several minutes with concentrated hydrochloric acid.

The hydrochloric acid dissolves out the tellurium dioxide and leaves the tellurium trioxide insoluble in water or acids. The tellurium trioxide was washed with dilute hydrochloric acid and finally with water. It was dried at 105° and kept in glass stoppered bottles for use.

The tellurium trioxide as prepared above was heated with the various anhydrous liquid chlorides in pressure tubes made

of heavy walled glass of 11 mm external diameter. One end of the tube was sealed with a rounded end and the other was heated to get a neck shaped tube, care being taken throughout the process to get a tube in which the walls were of even thickness and well annealed. About two grams of tellurium trioxide were introduced into the tube and the liquid poured in. The tube and its contents were cooled, and the end sealed off and annealed.

These tubes were heated for various lengths of time and at different temperatures in a tube furnace and the various changes noted. The tubes were cooled and opened by heating the top with a Bunsen burner. In several cases the pressure of the gas was so great that most of the material was lost. The liquid was poured off, the crystals washed several times with carbon bisulpide and dried between filter papers. These crystals were placed in small weighing bottles for analysis.

Carbon Tetrachloride.

Tellurium trioxide and carbon tetrachloride were heated together at various temperatures and for various lengths of time. The maximum was 200° for forty eight hours. No change took place in any case.

Phosphorus Trichloride.

Phosphorus trichloride reduces the tellurium trioxide at once to elementary tellurium. Heating up to 200° for forty eight hours does not change it further.

Phosphorus Oxychloride.

There was no action of the phosphorus oxychloride upon the tellurium trioxide in the cold. When heated to 100° for seven hours small white, flat crystals were obtained. On further heating at 200° for seven hours, all the tellurium trioxide went into solution and the liquid became clear. The temperature as well as the time of heating was varied but no further change was observed. The tube was finally opened and more tellurium trioxide added and heated at 200° for seven hours. This tellurium trioxide also went into solution and liquid was clear. On allowing the tube to stand at room temperature for several days, long white, flat crystals appeared.

Several other samples were prepared using larger amounts of tellurium trioxide. On heating these at 175° for seven hours the same kind of crystals were obtained.

Very little gas was given off when these tubes were opened. The odor of chlorine was present to a slight extent.

The crystals when analyzed gave the following results.

	Te	Cl	P
Calculated for $TeCl_4\ POCl_3$	30.15	58.71	7.35
1. Found " " "	31.00	57.51	7.38
2.	30.65	57.66	7.57
3.	31.05	57.94	6.81

It may be considered that the phosphorus oxychloride acts upon the tellurium trioxide to form tellurium tetrachloride, and this unites immediately with one molecule of the excess of phosphorus oxychloride forming an addition compound of tellurium tetrachloride and phosphorus oxychloride.

Arsenic Trichloride.

Arsenic trichloride has no action upon tellurium trioxide at room temperature. On heating to 100° for seven hours small needle like crystals appeared, but most of the trioxide was unchanged. Further heating gave no increase in the amount of crystals. A temperature of 150° for seven hours changed about three-fourths of the tellurium trioxide to crystals. A temperature of 175 to 200° changed all the tellurium trioxide to long needle like crystals in ten hours. There was no change in the appearance when the time of heating was prolonged.

No gas was liberated when the tubes were opened.

Analysis of the crystals -$TeCl_4$

	Te	Cl
Calculated	47.21	52.79
1 Found	50.10	51.05
2	49.69	50.86
3	50.53	49.24

There was no arsenic present in the crystals. The precipitates after weighing were dissolved and reprecipitated in order to check the first weighings.

Antimony Pentachloride.

Tellurium trioxide is not acted upon by antimony pentachloride at room temperature or when heated to 100°. When heated to 175° for seven hours all the tellurium trioxide went into solution with the formation of syrup-like liquid. The viscosity increased with the amount of tellurium trioxide in solution. It was impossible to get any crystals by heating. The tubes were then chilled in a freezing mixture for three days when large flat crystals appeared. These crystals were permanent at room temperature.Crystals were not obtained when only a small amount of tellurium trioxide was present.

Very little gas was given off when these tubes were opened. The odor of chlorine was noticed in several instances.

On washing the crystals with carbon bisulphide, a reddish appearance was given to them, which changed to a greyish yellow when dry.

The crystals on analysis gave the following results and indicated that an additional compound of $TeCl_4$ and $Sb\ Cl_5$ had formed.

	Te	Cl	Sb.
Calculated	22.49	56.35	21.16
1 Found	23.39	54.61	21.99
2	22.40	56.01	21.58

Sulphur Monochloride.

Sulphur monochloride acts slowly upon tellurium trioxide at room temperature giving small white crystals. This reaction was accelerated by heat. The sulphur monochloride completely changed all the tellurium trioxide in twenty four hours at 100°. On heating to 175° for six hours,long, white needle like crystals were formed. The tubes on being opened gave off a small amount of gas which fumed slightly in the air, indicating sulphur trioxide.

Analysis of the crystals showed the following composition. $TeCl_4$.

	Te	Cl
Calculated	47.21	52.79
1 Found	47.66	52.24
2	47.73	51.93

No sulphur was found in the samples.

Thionyl Chloride.

Tellurium trioxide is acted upon slowly by thionyl chloride at room temperature. A temperature of 100° in two hours changed about one-fourth of the tellurium trioxide to short needle like crystals. Increasing the length of time of heating did not materially increase the amount of crystals produced. A temperature of 200° for four hours changed all the tellurium trioxide into long white, needle like crystals.

The tubes gave a great deal of gas on being opened and some fumes of sulphur trioxide.

Tellurium tetrachloride was formed by the reaction.

	Te	Cl.
Calculated	47.21	52.79
1 Found	47.82	51.85
2	47.41	51.90
3	47.31	52.69

No sulphur was found in the samples.

Sulphuryl Chloride.

Sulphuryl chloride and tellurium trioxide when heated together for seven hours at 100° gave a few needle like crystals floating in the solution, while the rest of the tellurium trioxide was reduced to tellurium dioxide. On heating to 200° for seven hours long needle like crystals appeared throughout the entire liquid.

One tube did not act the way the others did. On heating to 200° for six hours, some material still remained on the bottom of the tube and looked like tellurium dioxide, but no crystals were present. On heating a longer time at 200° the white material dissolved forming a colorless liquid. This liquid would not mix with the excess of sulphuryl chloride. After heating twenty four hours at 200°, this oily liquid disappeared and the solution became clear and homogeneous. There were no crystals present in the solution and further heating brought no change. On chilling the tube for several days in a freezing mixture no crystals separated.

On opening the tube to add more tellurium trioxide, chlorine was given off. When a very small amount of the tellurium trioxide touched the surface of the liquid a violent evolution of gas resulted and the liquid was rapidly ejected from the tube. A promounced odor of chlorine was noted. This was the only tube that acted thus. All the rest of the series gave long needle-like crystals and chlorine when opened.

The sulphuryl chloride formed addition compounds of various composition depending upon the amount of tellurium trioxide present. Their composition from the data obtained

would be $TeSCl_3$ or $TeO_2 SO_2 Cl_2 Cl$

Te	Cl	S
34.75	27.70	8.20
34.66	29.83	8.72

Methods of Analysis.

Separate samples were used for the tellurium and chlorine determinations. When sulphur was determined the filtrate from the chlorine precipitation was used and the tellurium filtrate for the phosphorus and antimony.

On account of the hydroscopic nature of the crystals only enough sample was placed in a weighing bottle for one determination. The samples were weighed by difference and poured directly into a beaker containing water.

Tellurium

The tellurium was determined according to the method of Lenher and Homberger[1]. The sample was introduced into a beaker containing a 10 percent hydrochloric acid solution. The solution was warmed, 10cc. of a saturated solution of sulphur dioxide were added, then 10cc. of a 15 percent solution of hydrazine hydrochloride and again 25 cc. of a saturated solution of sulphur dioxide. The solution was boiled for about five minutes and filtered on a porcelain Gooch filter then washed with hot water to remove the chlorides. The water was displaced with alcohol and contents dried at 105°.

Chlorine

The sample for the chlorine determination was dissolved in a solution containing nitric and tartaric acids. The solution was brought to boiling and silver nitrate added slowly with constant stirring to prevent the tellurium from coming

1- Lenher and Homberger. J.A.C.S. 30 387.

down as a tellurite of silver. The tartaric acid was added to hold the tellurium in solution. The solution was allowed to stand over night and filtered on a porcelain Gooch filter, washed with hot (dilute) nitric acid and the water displaced by alcohol. The precipitate was dried at 105°. The chlorine factor used was .24737.

Phosphorus.

The filtrate from the tellurium precipitation was boiled free of sulphur dioxide and bromine water was added to oxidize the phosphorus to phosphorus pentoxide. The solution was neutralized with ammonium hydroxide and magnesium mixture added in order to precipitate the phosphate as magnesium ammonium phosphate. This magnesium ammonium phosphate precipitate was brought upon a Gooch filter, washed with dilute ammonium hydroxide, dried and ignited to constant weight as magnesium pyrophosphate. The phosphorus was calculated from the magnesium pyrophosphate by the factor .27867.

Antimony.

The antimony was determined in the tellurium filtrate. The sulphur dioxide was boiled out, the solution was cooled and hydrogen sulphide passed in. The solution was gradually brought to boiling, the antimony precipitating as antimony trisulphide. The precipitate was washed with dilute hydrochloric acid, next carbon bisulphide and finally with alcohol. The crucible and contents were dried at 105° and the antimony calculated by the factor .7136.

Conclusions.

From the date obtained it appears that three series of salts are formed. (1) Tellurium tetrachloride only as by the action of arsenic trichloride, sulphur monochloride and thionyl chloride. (2) Addition compounds of definite composition as are formed by tellurium tetrachloride and the reagent such as phosphorus oxychloride and antimony pentachloride. (3) Addition compounds of indefinite composition as by action of sulphuryl chloride.

The resulting compounds are the same as those obtained by the action of these various chlorides on tellurium and on tellurium dioxide.

Tellurium tetrachloride- White needle like crystals, decomposed by water to form tellurous acid and hydrochloric acid.

Tellurium tetrachloride and phosphorus oxychloride- large flat monoclinic crystals.

Tellurium tetrachloride and antimony pentachloride- large flat crystals arranged in layers.

Tellurium trioxide and sulphuryl chloride- crystals were large and irregular forming a sort of mass in the bottom of the tube.

Approved. Victor Lenher

Date. July 30, 1917

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